Academician A. N. FRUMKIN, L. I. BOGUSLAVSKII, and V. S. SEREBRENNIKOV

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Abstract

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Academician A. N. FRUMKIN, L. I. BOGUSLAVSKII, and V. S. SEREBRENNIKOV

ON THE ELECTRODE BEHAVIOR OF THERMALLY TREATED POLYACRYLONITRILE

Recently it has been shown ([1,2,3]) that organic semiconductors are catalysts for certain oxidation-reduction reactions. It was of interest to investigate their influence on the kinetics of electrochemical processes, taking into account, in particular, that there exists a well-known parallelism between the ability to assume an oxygen potential and activity with respect to the decomposition reaction of hydrogen peroxide. In connection with this, we studied the electrochemical behavior of thermally treated polyacrylonitrile, which, according to the data of A. V. Topchiev, M. A. Geiderikh, and others ([1]), is a catalyst for the decomposition reaction of hydrogen peroxide. All electrochemical characteristics of polyacrylonitrile were compared with the properties of carbon obtained by carbonization of viscose.

The specimens studied consisted of yarns made up of several hundred filaments, 2–3 μ thick. Special attention was paid to preventing the solution from reaching the contact of the polyacrylonitrile with the platinum wire to which the specimen was attached. For this purpose the middle part of the specimen was impregnated with paraffin. In alkali the potential was measured relative to a normal oxygen-mercury electrode, and in acid relative to a normal sulfate electrode.

Figure 1 gives curves showing the change in potential as a function of the logarithm of the current strength for specimens of the polymer and of carbon in a hydrogen atmosphere in $1\,N\ H_2SO_4$. As can be seen, the electrochemical activity of the material studied with respect to the cathodic and anodic processes is considerably lower than the activity of carbon. It remains unclear whether, under anodic polarization, ionization of molecular hydrogen occurred at all, or whether the current went to the oxidation of the organic substance or of residues of hydrogen adsorbed during the cathodic polarization that preceded the anodic one.

A different picture is obtained when the polymer is polarized in an atmosphere of air, as is seen from Figs. 2 and 3, which give the curves obtained in $1\,N\ H_2SO_4$ and $1\,N$ NaOH. In this case the activities of the polymer and of carbon prove to be quantities of the same order.

It should be noted that all processes occurring on the polymer have a substantially nonstationary character. At constant current the potential changes con-

Fig. 1. Dependence of the potential on the logarithm of the current for specimens of polymer and carbon in a hydrogen medium in 1 N H_2SO_4 under anodic and cathodic polarization. 1 —polymer, 2 —carbon.

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Fig. 2. Dependence of the potential on the logarithm of the current for specimens of polymer and carbon in air in 1 N H_2SO_4 under anodic and cathodic polarization. 1 —carbon, 2 —polymer.

Figure 2: Fig. 2. Dependence of the potential on the logarithm of the current for specimens of polymer and carbon in air in 1 N H_2SO_4 under anodic and cathodic polarization. 1 —carbon, 2 —polymer.

tinuously in the direction of increasing polarization. In order to reduce concentration polarization with respect to oxygen, current-voltage curves were taken on a rotating electrode in 1 *N* NaOH; however, changing the rotation rate from several hundred to several thousand revolutions per minute did not substantially affect the form of the polarization curves. The nonstationarity observed in experiments without stirring is not eliminated by means of a rotating electrode. Apparently, it is connected with depletion of oxygen from the solution in the micropores of the specimens. The most interesting results were obtained in measuring the stationary potentials assumed by polymers in an oxygen atmosphere in 1 *N* NaOH. With some specimens, potentials of +0.280-0.285 relative to the normal oxygen-mercury electrode were observed, which is only 25-30 mV ...

more negative than the reversible oxygen potential for the water-formation reaction. These potentials are considerably more positive than the oxygen potentials that were observed on electrodes made of activated carbon, smooth platinum, or platinized platinum. Only in ultrapure solutions of H_2SO_4 were Bockris and Huq (4) apparently able to attain the value of the reversible oxygen potential on platinum. With time, the potential of the polymer electrode becomes more negative, shifting by 90 mV in 1 h and by 120 mV in 30 h.

Fig. 1. Dependence of the potential on the logarithm of the current for specimens of polymer and carbon in a hydrogen medium in 1 N H_2SO_4 under anodic and cathodic polarization. 1 —polymer, 2 —carbon.

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It is evident that establishment of the reversible oxygen potential presupposes the reversibility of all stages of oxygen ionization, and first of all the stage of adsorption of the O_2 molecule. Thus, the electrochemical behavior of the

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

materials studied must be associated not only with their ability to catalyze the transition from hydrogen peroxide to water, but also with the ability to form on the surface easily detach—

···labile peroxides that liberate oxygen, which is indeed characteristic of many polymers with conjugated double bonds. The gradual transition from this primary stage of oxidation to more stable forms of oxygen bonding may be one of the reasons for the incomplete reversibility of the electrode.

Fig. 3. Dependence of the potential on the logarithm of the current for specimens made of polymer and carbon in air in 1 N NaOH under anodic and cathodic polarization.
1 —polymer, 2 —carbon

In view of the fact that O. V. Krylov and S. Z. Roginskii [5] investigated the effect of the width of the forbidden band on the rate of the decomposition reaction of isopropyl alcohol in the series ZnO—ZnTe and found a sharp increase in catalytic activity with decreasing forbidden-band width, we tested polymer filaments with a smoothly varying activation energy of conductivity, determined from the dependence of conductivity on reciprocal temperature. The values of the activation energy were measured at the Institute of Semiconductors of the Academy of Sciences of the USSR in the laboratory of L. S. Stil' bans. The potential established on the polymer in 1 N NaOH in an atmosphere of air depends on the magnitude of the activation energy, as shown in Fig. 4.

Fig. 4. Dependence of the potential on the activation energy of conductivity ΔE

It turned out that the value of the potential maximum differs from the minimum value by approximately 100 mV, which corresponds to a change in the reaction rate by 3 orders of magnitude, although there is considerable scatter of the experimental values. The observed maximum of catalytic activity may be related to the specificity of organic catalysts in biochemical systems.

Institute of Electrochemistry
Academy of Sciences of the USSR

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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